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(54) Title: SHELL MOLD BINDER COMPOSITION AND METHOD

(57) Abstract: The invention provides a composition that significantly shortens the time necessary to produce a ceramic shell mold. The composition of the invention is used to produce a shell-mold for the investment casting process, providing decreased processing times by reducing the number of shell dips, and better handling and dewaxing through increased green strength. The invention provides a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising 0.1 to 70 percent by weight inorganic fibers providing a disposable pattern, applying said composition to said pattern to form a binder coated pattern, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating, the improvement wherein said binder composition comprises. The invention provides in a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; providing a disposable pattern, applying said composition to said pattern to form a binder coated pattern, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating, the improvement wherein the binder composition comprises 0.1 to 70 percent by weight of inorganic fibers.

## SHELL MOLD BINDER COMPOSITION AND METHOD

## FIELD OF THE INVENTION

This invention relates to water based back-up binder composition comprising colloidal silica and polymer(s) and the use thereof to create rapid-processing slurry for making shell molds. The back-up binder composition of the invention includes fibers and is used to quickly make ceramic shell molds for investment casting processes. Prior art binder compositions do not include fibers. The invention provides a composition that significantly shortens the time necessary to produce a ceramic shell mold. The composition of the invention, when used to produce a shell-mold for the investment casting process, not only provides for decreased processing times by reducing the number of shell dips, but also provides for better handling and dewaxing through increased green strength.

Producing a shell-mold for investment casting usually includes dipping a wax replica (or model) into a slurry containing a binder and a refractory powder. The slurry coats the wax, and excess slurry is allowed to drain off. A coarser refractory is sprinkled onto the wet wax pattern, and this combination is allowed to dry. Additional coatings of slurry and refractory are applied by the same method until the mold has sufficient thickness and strength for further processing. A primary coat is defined as the initial one or two coats applied to the wax pattern or model. The purpose of the primary coats is to provides a surface with a high refractoriness for the metal to be cast against and to duplicate the detail of the model. Primary binders are colloidal silica based and normally contain other additives such as wetting agents, anti-foam agents and polymers. The refractory flour is typically 200 - 400 mesh and is normally zircon but could also contain some fused silica. Zircon is chosen due to its excellent refractory properties. The stucco materials for primary coats are typically finer (50 - 150 mesh) to help capture the detail of the model. The stucco material for primary coats is typically zircon but could be fused silica. Backup coats are normally applied to the pattern after the primary coats. A seal coat is a slurry coat only, no stucco is applied. This seal coat is commonly added by the

industry to "seal" loose stucco to the pattern. The main purpose of the backup coats is to provide the shell adequate strength to withstand the forces and pressures that will be exerted on it in the process of producing a casting. A seal coat is applied after the final backup coat. The main stress is due to the pressure exerted on the shell by the wax during the wax removal process. The number of backup coats required for each shell depends on the size of the overall mold as well as the amount of alloy that will be poured into the shell.

It is a common practice in the field of investment casting to characterize the green (unfired) properties of a shell mold (the properties prior to firing) by the 3-point bending, where a single point load is gradually applied to a green shell test piece, supported on two stationary points, until it fractures. One major interest of the bending test is to acquire one measure of the shell material green strength: the Modulus of Rupture (MOR).

Modulus of Rupture (MOR), as used herein is defined by the following formula:

$$MOR = (3 \times L_f \times S) / (2 \times W \times T^2)$$

Where  $L_f$  is the maximum load at fracture, S the span between the two stationary points and W and T the width and thickness of the test bar respectively, as set forth in Investment Casting Institute Ceramic test procedure 770-79 (1979). MOR is an intrinsic material property, thus, a property regardless of the physical dimensions of the test bar. Knowing that shell thickness is a major factor determining the actual shell performance when the shell is subjected to an external load, adjusted fracture load (AFL), which takes into account the thickness, is a more realistic measure of the shell strength. AFL information and formulas have been published in numerous industry papers.

Adjusted fracture load (AFL) as used herein is defined by the following formula:

$$\text{AFL} = [f_x(\text{MOR})_x T^2]$$

Where  $f$  is a constant factor determined by the type of bending as set forth in "Faster and Safer Shell Production" by Carl Schwartz of Ransom & Randolph in 1988.

"Polymer" in shell-mold for investment casting generally refers to a macromolecule formed by the chemical union of 5 or more identical combining units called monomers. The polymer types used in this invention are known as elastomers. An elastomer is a polymer possessing elastic properties.

Refractory, as used herein refers to inorganic particulate material useful in making shell-molds for investment casting. Refractory material is resistant to change, especially during the application of heat. The main refractories used in the industry are as follows: Zircon:  $\text{ZrSiO}_4$  (Zirconium Silicate), Alumina:  $\text{Al}_2\text{O}_3$  (Aluminum oxide), Silica:  $\text{SiO}_2$  (Silicon Dioxide) and Alumino-silicate:  $x \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$ . Blends of alumina and silica that have usually been fired to high temperature (2500°F.) to form a stable phase known as mullite, and to minimize shrinkage due to firing. These refractories are in two forms: one form is the form of a powder, and the other form is the form of a coarser sand, usually called stucco. Both the powders and stuccos can vary in their sizes, according to the respective application.

Refractory powder (or refractory flour), as used herein refers to refractory particulate material having a particle size such that at least 60 percent of the particles are smaller (finer) than 100 mesh. Preferably refractory powder (or refractory flour) is refractory particulate material having a particle size such that at least 90 percent of the particles are smaller (finer) than 100 mesh.

Refractory sand, (or refractory stucco) as used herein refers to refractory particulate material having a particle size that at least 60 percent of the particles are larger (coarser) than 100 mesh. Preferably refractory sand, (or refractory

stucco) is refractory particulate material having a particle size such that at least 90 percent of the particles are larger (coarser) than 100 mesh.

"Latex Polymer" as used herein refers to an elastomeric polymer in water. For example elastomeric polymer of the styrene butadiene (S/B type) group and the elastomeric polymer of the acrylic group typically have the following properties:

LATEX #	PH	SOLIDS Percent	Specific viscosity (centipoise)	Specific gravity (g/ml)	TYPE
100	8-9	53%	N/A	1.01	S/B
101	6-7	50%	N/A	1.01	S/B
120	8.5	50%	200	1.03	Acrylic
121	7.0	50%	40	1.01	Acrylic
140	9.5	47%	100	1.05	Acrylic

"Colloidal Silica" in shell-mold for investment casting generally refers to an aqueous dispersion of minute silica particles, usually employing a small amount of a strong base (e.g., ammonia or sodium hydroxide) as a stabilizer to yield a stable suspension. The resulting pH is typically in the 8.0-11.0 range.

"Dewaxing" refers to removal of wax from within an unfired mold coating to from an unfired mold, which is then fired and used in investment casting.

"Primary coating" refers to an initial coating of slurry and stucco material adapted to record minute surface details and formed, as is known in the art, from a slurry formed from Primcote® binder material manufactured by Ransom & Randolph, and typically coated on a wax model by dipping in a slurry thereof.

"Inorganic fibers" as used herein refers to fibers having a length to width ratio of at least 10, more preferably 30, comprising inorganic material, and more preferably consisting essentially of inorganic material.

It is an object of the invention to provide a method of forming a shell mold, comprising providing an investment casting shell-mold composition wherein a polymer and fiber free binder and flour pattern coating is formed in the same manner as the binder and flour pattern coating except without the polymer and fibers, the fiber and polymer free binder and flour pattern coating has a fiber and polymer free green MOR and a polymer and fiber free green AFL, the binder and flour pattern coating has a polymer and fiber containing green MOR and a polymer and fiber containing green AFL, the polymer and fiber containing green MOR is at least 50 percent greater than the polymer and fiber free green MOR, the polymer and fiber containing green AFL is at least 150 percent greater than the polymer and fiber free green AFL at the same number of coats, and, at at least 40 percent of coat reduction, the polymer and fiber containing green AFL is equal to the polymer and fiber free green AFL.

It is an object of the invention to provide a method of forming a shell mold, comprising providing an investment casting shell-mold composition wherein a polymer containing but fiber free binder and flour pattern coating is formed in the same manner as the binder and flour pattern coating except without the fibers, the polymer containing but fiber free binder and flour pattern coating has a polymer containing but fiber free green MOR and a polymer containing but fiber free green AFL, the binder and flour pattern coating has a polymer and fiber containing green MOR and a polymer and fiber containing green AFL, the polymer and fiber containing green MOR is at least 25 percent greater than the polymer containing but fiber free green MOR, and the polymer and fiber containing green AFL is at least 100 percent greater than the polymer containing but fiber free green AFL at the same number of coats, and, at at least 25 percent of coat reduction, the polymer and fiber containing green AFL is equal to the polymer containing but fiber free green AFL.

It is an object of the invention to provide a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising 0.1 to 70 percent by weight inorganic fibers providing a disposable

pattern, applying the composition to the pattern to form a binder coated pattern, applying refractory flour to the binder coated pattern to form a binder and flour pattern coating, the improvement wherein the binder composition comprises.

It is an object of the invention to provide in a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; applying refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory layer (stucco) the improvement wherein the binder composition comprises 0.1 to 70 percent by weight of inorganic fibers.

It is an object of the invention to provide an investment casting shell-mold composition comprising: a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers; wherein the inorganic particles have an average particle size smaller than 600 mesh, and the inorganic fibers have an average length to diameter ratio of more than 30.

It is an object of the invention to provide a method of forming a shell mold, comprising the steps of providing an investment casting shell-mold composition comprising: a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers; wherein the inorganic particles have an average particle size smaller than 600 mesh, and the inorganic fibers have an average length to diameter ratio of more than 30, applying refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory layer (stucco).

## SUMMARY OF THE INVENTION

The invention provides a composition that significantly shortens the time necessary to produce a ceramic shell mold. The composition of the invention, when used to produce a shell-mold for the investment casting process, not only provides for decreased processing times by reducing the number of shell dips, but also provides for better handling and dewaxing through increased green strength.

The invention to provide a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising 0.1 to 70 percent by weight inorganic fibers providing a disposable pattern, applying the composition to the pattern to form a binder coated pattern, applying refractory flour to the binder coated pattern to form a binder and flour pattern coating, the improvement wherein the binder composition comprises.

The invention provides an investment casting shell-mold composition comprising: a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers; wherein the inorganic particles have an average particle size smaller than 600 mesh, and the inorganic fibers have an average length to diameter ratio of more than 30.

The invention provides an improvement in a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; mixing refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory layer (stucco); the improvement wherein the binder composition comprises 0.1 to 70 percent by weight of inorganic fibers.

The invention provides a method of forming a shell mold, comprising the steps of providing an investment casting shell-mold composition comprising: a



binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers; wherein the inorganic particles have an average particle size smaller than 600 mesh, and the inorganic fibers have an average length to diameter ratio of more than 30, applying refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory layer (stucco).

The invention provides a method of forming a shell mold, comprising providing an investment casting shell-mold composition wherein a polymer and fiber free binder and flour pattern coating and a polymer containing but fiber free binder and flour pattern coating are formed in the same manner as the binder and flour pattern coating except without the fibers and polymer and without the fibers, the polymer and fiber free binder and flour pattern coating has a polymer and fiber free green AFL, the polymer containing but fiber free binder and flour pattern coating has a polymer containing but fiber free green AFL, the binder and flour pattern coating has a polymer and fiber containing green AFL, at the same number of coats, the polymer and fiber containing green AFL is at least 150 percent greater than the polymer and fiber free green AFL and at least 100 percent greater than the polymer containing but fiber free green AFL.

#### DETAILED DESCRIPTION OF THE INVENTION

In general, the binder in accordance with the invention may be used to make a shell-mold according to the following process. The binder preferably includes a mixture of a colloidal sol, inorganic fiber and a latex polymer. A refractory powder is added to the binder to make a slurry, and the slurry is mixed to wet-out the powder. A disposable pattern of material such as a wax pattern is dipped into the slurry, the excess slurry is drained off, and the pattern is stuccoed with an additional refractory while it is still wet. The pattern and slurry are dried to set bonds in the binder.

The dipping, draining, and stuccoing steps may be repeated as necessary to build up a shell mold having a predetermined, desired thickness. After the mold is completed, the disposable pattern is eliminated by heating and draining the liquid pattern material, and the shell mold is fired. After firing, molten metal is poured into the shell mold and allowed to cool. After cooling, the shell mold is broken off from the metal to provide a desired cast metal component.

The latex polymer or polymers are present in the binder to increase the green strength properties of the shells made from the binder. Additionally the latex polymer or polymers reduce the processing time between dips, compared to dips made with binders without the latex polymers or polymers, during the mold making process. The inorganic fibers are present to increase the thickness of each coat of binder containing latex polymer or polymers, thus creating a sufficiently strong shell, of similar thickness, in less coats compared to other existing binders.

Colloidal silica sols which are preferred for use in this invention have average particle sizes of 3 to 100 nanometers (nm), more preferably 5-20 nm, and have a silica content of 8-50% (by weight), and preferably 12-35%. There are many types of latexes, such as vinyl acetates, polyvinylidene chlorides, acrylics, styrene butadienes, etc. The styrene butadiene latexes have received the most attention in investment casting, as many of these possess good compatibility when mixed with colloidal silica, and can add to improved shell green strength. A preferred latex polymer includes a blend of acrylic polymers with the following properties: a pH in the range of 6-11 (most preferably 7-10); a viscosity in the range of 50-1000 centipoise (most preferably 50-500); a solids content of 40-65% (most preferably 45-55%); and an average particle size of 0.05-1.0 microns (most preferably 0.1-0.5 microns). Preferred inorganic fibers for use in accordance with the invention have an average length to diameter ratio of more than 30. Examples of refractory flours (or powders) commonly used in the investment casting industry are zircon ( $\text{ZrSiO}_4$ ), fused silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), zirconia ( $\text{ZrO}_2$ ), and alumino-silicate (various combinations of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , usually fired to high temperatures, 2500 degree F). Any other compatible powder system can also

be used. The sizes of the powders used are typically classified as -120 mesh (U.S.A. Standard Sieves) to -400 mesh. The sizes normally used are well known to those skilled in the art, and other sizes are not excluded from the scope of this invention. The slurry preferably will have a viscosity in the range of 5 to 50 seconds, as measured by a #4 Zahn cup.

The latex polymer is added to the colloidal silica base in any proportion such that the ratio of colloidal silica to latex polymer(s) is greater than 1:1, and preferably greater than 3:1. The concentration of colloidal silica would be expected to be between 8% and 80% by weight of the composition. It is preferred that the latex polymer be present in an amount of 2 to 20% by weight, based on the binder weight. Other ingredients (surfactants, biocides, etc.), well known to those skilled in the art, can also be added to the binder without altering the spirit and scope of this invention. Refractory flour is mixed with the binder to form a slurry. To a primary coated disposable pattern is applied the slurry composition to form a slurry coated pattern. A dry coarse refractory layer (stucco) is applied to the slurry coated pattern. A stucco coated pattern is formed by repeatedly drying, dipping, draining, stuccoing and drying.

A preferred embodiment the invention provides in a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; applying refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory layer (stucco). The improvement is that the binder composition comprises 0.1 to 70 percent by weight of inorganic fibers. A polymer and fiber free binder and flour pattern coating is formed in the same manner as the binder and flour pattern coating except without the polymer and fibers. The polymer and fiber free binder and flour pattern coating has a polymer and fiber free green AFL. The binder and flour pattern coating has a polymer and fiber containing green

AFL. At the same number of coats, the polymer and fiber containing green AFL is preferably at least 75 percent greater than the polymer and fiber free green AFL. The polymer and fiber containing green AFL is more preferably at least 100 percent greater than the polymer and fiber free green AFL. The polymer and fiber containing green AFL is most preferably at least 150 percent greater than the polymer and fiber free green AFL. Another polymer containing but fiber free binder and flour pattern coating is formed in the same manner as the binder and flour pattern coating except without the fibers. The polymer containing but fiber free binder and flour pattern coating has a polymer containing but fiber free green AFL. At the same number of coats, the polymer and fiber containing green AFL is preferably at least 50 percent greater than the polymer containing but fiber free green AFL. The polymer and fiber containing green AFL is more preferably at least 75 percent greater than the polymer containing but fiber free green AFL. The polymer and fiber containing green AFL is most preferably at least 100 percent greater than the polymer containing but fiber free green AFL.

A preferred embodiment the invention provides an investment casting shell-mold composition comprising: a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers. The inorganic particles have an average particle size smaller than 600 mesh, and the inorganic fibers have an average length to diameter ratio of more than 30.

A preferred embodiment the invention provides a method of forming a shell mold, comprising the steps of providing an investment casting shell-mold composition comprising: a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers. The inorganic particles have an average particle size smaller than 600 mesh, and the inorganic fibers have an average length to diameter ratio of more than 30.

Refractory flour is mixed with the binder to form a slurry. A primary coated disposable pattern, is coated with the slurry composition to form a slurry coated pattern. The slurry coated pattern is formed by repeatedly dipping the primary coated disposable pattern in the slurry composition, draining, and drying. A stucco coated pattern is formed by stuccoing (applying dry coarse refractory layer) and drying the slurry coated pattern.

In accordance with a preferred embodiment of the invention is provided an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers. The inorganic particles have an average particle size smaller than 600 mesh, said inorganic fibers having an average length to diameter ratio of more than 30. Preferably the binder composition includes 1 to 90 percent by weight refractory powder. Preferably the refractory powder has a mesh size in the range of 120 to 400 mesh and said refractory powder is selected from the group consisting of alumino-silicates, fused silica, quartz silica, alumina, zircon, and zirconia. Preferably the colloidal sol comprises silica having an average particle diameter of 3 to 100 nanometers. Preferably the ratio of colloidal silica to latex polymer is greater than 1:1. Preferably the ratio ranges from 10:1 to 1:1, colloid:latex. Preferably the latex polymer includes a blend of acrylic polymers having a pH in the range of from 6 to 11; a viscosity in the range of from 50 to 1000 centipoise; a solids content of from 40 to 65percent; and an average particle size of from 0.05 to 1.0 microns. Preferably the latex polymer includes a blend of acrylic polymers having a pH of from 7 to 10; a viscosity of from 50 to 500; a solids content of from 50 to 60percent; and an average particle size of from 0.1 to 0.5 microns. Preferably the polymer latex is an acrylic latex or a styrene butadiene latex. Preferably the silica sol has an average particle size of less than 30 nanometers. Preferably the latex polymer is an elastomeric latex polymer. Preferably the binder composition include from 1 to 98 percent by weight water.

In accordance with a preferred embodiment of the invention is provided a method of forming a shell mold, comprising the steps of providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and 0.1 to 70 percent by weight of inorganic fibers. The inorganic particles having an average particle size smaller than 600 mesh, said inorganic fibers having an average length to diameter ratio of more than 30. Then refractory flour is mixed with the binder composition to form a slurry composition, and applied to a pattern, to form a slurry coating on the pattern. Then refractory stucco is applied to the slurry coating to form a slurry and stucco pattern coating. Preferably the refractory flour has a particle size of from 120 to 400 mesh.

In accordance with a preferred embodiment of the invention is provided in method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a liquid binder composition; mixing refractory flour with the binder to form a slurry composition, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a partial slurry coating on said pattern, draining at least a portion of said liquid from said partial slurry coating to form a drained partial slurry coating. Then applying the slurry composition to said drained partial slurry coating to form a wet slurry coating, draining at least a portion of said liquid from said wet slurry coating to form a drained slurry coating and applying refractory stucco material to said drained slurry coating to form a refractory stucco and slurry coating, the improvement wherein said liquid binder composition comprises 0.1 to 70 percent by weight of inorganic fibers. Preferably the liquid binder composition further comprises 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and said refractory flour comprises inorganic particles having an average particle size smaller than 600 mesh. Preferably the inorganic fibers have an average length to diameter ratio of more than 30. Preferably the applying said composition to said pattern to form a slurry coated pattern, and said applying refractory stucco to said slurry coated pattern are repeated after drying.

In accordance with a preferred embodiment of the invention is provided a method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising 0.1 to 70 percent by weight inorganic fibers, providing a disposable pattern, applying said composition to said pattern to form a binder coated pattern, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating, the improvement wherein said binder composition comprises. Preferably the investment casting shell-mold composition further comprises 1-20 percent by weight organic polymer.

In accordance with a preferred embodiment of the invention is provided a shell mold formed by the process comprising: providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; and 0.1 to 70 percent by weight of inorganic fibers applying refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory stucco layer.

In accordance with a preferred embodiment of the invention is provided in method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a back-up binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; providing a disposable pattern, applying said composition to said pattern to form a binder coated pattern having a binder coating, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating, the improvement comprising adding 0.1 to 70 percent by weight of inorganic fibers to said back-up binder composition to form a fiber containing back-up binder composition . Preferably a back-up binder composition has a green Modulus of Rupture (MOR), and said fiber containing back-up binder composition has a green Modulus of Rupture (MOR) at least 25 percent greater than said back-up binder composition green Modulus of Rupture (MOR). Preferably the back-up binder composition has a green adjusted fracture

load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 75 percent greater than said back-up binder composition green adjusted fracture load (AFL). Preferably the back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 75 percent greater than said back-up binder composition green adjusted fracture load (AFL). Preferably a fiber free binder coating is formed as said binder coating except without said fiber, and is at least 25 percent thinner than said binder coating formed from said fiber containing back-up binder composition. Preferably the back-up binder composition has a green Modulus of Rupture (MOR), and said fiber containing back-up binder composition has a green Modulus of Rupture (MOR) at least 35 percent greater than said back-up binder composition green Modulus of Rupture (MOR). Preferably the back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 100 percent greater than said back-up binder composition green adjusted fracture load (AFL). Preferably the back-up binder composition has a green Modulus of Rupture (MOR), and said fiber containing back-up binder composition has a green Modulus of Rupture (MOR) at least 50 percent greater than said back-up binder composition green Modulus of Rupture (MOR). Preferably the back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 150 percent greater than said back-up binder composition green adjusted fracture load (AFL). Preferably a fiber free binder coating is formed as said binder coating except without said fiber, and said fiber free binder coating is at least 33 percent thinner than said binder coating formed from said fiber containing back-up binder composition. Preferably a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Modulus of Rupture and said binder and flour pattern coating has a fiber containing green Modulus of Rupture at least 50 percent greater than said fiber free green Modulus



of Rupture. Preferably a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Adjusted Fracture Load and said binder and flour pattern coating has a fiber containing green Adjusted Fracture Load at least 150 percent greater than said fiber free green Modulus of Rupture. Preferably a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Modulus of Rupture and said binder and flour pattern coating has a fiber containing green Modulus of Rupture at least 25 percent greater than said fiber free green Modulus of Rupture. Preferably a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Adjusted Fracture Load and said binder and flour pattern coating has a fiber containing green Adjusted Fracture Load at least 100 percent greater than said fiber free green Modulus of Rupture.

In accordance with a preferred embodiment of the invention is provided a shell mold formed by the process comprising: providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; and 0.1 to 70 percent by weight of inorganic fibers applying said composition to a pattern to form a binder coated pattern, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating and firing said binder and flour pattern coating to form a shell mold.

In accordance with a preferred embodiment of the invention is provided a green shell mold formed by the process comprising: providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of inorganic particles, 1-20 percent by weight organic polymer; and 0.1 to 70 percent by weight of inorganic fibers, mixing refractory flour and the binder to form a slurry composition, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a wet slurry coating on said pattern, draining at least a portion of said water from said wet slurry coating to form a drained slurry coating, applying a coarse refractory

stucco to said drained slurry coating and removing said pattern from said drained slurry coating to form a green shell mold.

The following Examples described preferred embodiments of the claimed invention. These Examples should be construed as illustrating the claimed invention, and not as limiting the same.

**EXAMPLE 1: back-up binder composition**

60.29 grams colloidal silica ( $\text{SiO}_2$ : 10 nanometers average particle diameter); 18.96 grams deionized water; 15.57 grams acrylic polymer emulsion: 55 percent by weight acrylic polymer; 45 percent by weight water; (Duramax TM B 1000); 1.46 grams inorganic fibers ( $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) having a median length of 650  $\mu\text{m}$ ; median diameter of 8.5  $\mu\text{m}$  and average length to diameter (aspect) ratio of 80 and a composition of: 46 percent by weight  $\text{SiO}_2$ ; 15 percent by weight  $\text{Al}_2\text{O}_3$ ; 16 percent by weight  $\text{CaO}$ ; 12 percent by weight  $\text{MgO}$ ; 6 percent by weight  $\text{FeO}$  and 5 percent by weight impurities. The binder composition is mixed with refractory flour to form a binder and flour slurry. The refractory flour has particle size of between 120 mesh and 325 mesh. The refractory flour is fused  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3 \bullet \text{SiO}_2$ .

**EXAMPLE 2**

A wax model is dipped into a primary slurry for the initial coating of refractory material to form a coated wax model. The coated wax model is dipped into the binder and flour slurry formed by following the procedure of EXAMPLE 1, for about five seconds. Then the wax model is lifted from the slurry and allowed to drain for some 30-60 seconds. The wax model with the drained slurry layer is then coated with coarse sand by dipping it into a fluid bed of sand for about five seconds or by use of a rainfall sander that sprinkles the stucco over the pattern. The sand is composed of fused  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3 \bullet \text{SiO}_2$ . The mesh size of the sand is between 30 and 100 mesh. This procedure is repeated three times to form a coat of a width about 5 mm thickness. The coated wax model is then

heated to melt and then remove the wax and the mold formed is then fired at a temperature between 1600 and 2000°F for from about 1 to 3 hours. The finished mold is then used by pouring liquid metal into the mold allowing the metal to cool and then removing the mold from the cooled metal. The metals which may be molded include iron, aluminum, nickel and alloys thereof.

### EXAMPLE 3

60.85 grams colloidal silica ( $\text{SiO}_2$ : 10 nanometers average particle diameter); 19.64 grams deionized water; 15.71 grams acrylic polymer emulsion: 55 percent by weight acrylic polymer; 45 percent by weight water; (Duramax TM B 1000); 1.47 grams alkoxylated primary alcohol; LF-60 MOD (wetting agent) manufactured by DeForest Enterprises Inc.; 0.49 grams silicone emulsion DCH-10 (defoamer) manufactured by Dow Corning; 0.02 grams broad spectrum bactericide; GROTAN (biocide) manufactured by US Professional Labs, 0.02 grams hydroxy compound; ammonia mask (fragrance) manufactured by Alpine Aromatics International Inc., 1.8 grams inorganic fibers ( $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) having a median length of 650  $\mu\text{m}$ ; median diameter of 8.5  $\mu\text{m}$  and average length to diameter (aspect) ratio of about 80 and a composition of: 46 percent by weight  $\text{SiO}_2$ ; 13.5 percent by weight  $\text{Al}_2\text{O}_3$ ; 17.7 percent by weight  $\text{CaO}$ ; 9.7 percent by weight  $\text{MgO}$ ; 7 percent by weight  $\text{FeO}$  and 6.1 percent by weight others. The binder composition is mixed with refractory flour. The refractory flour has particle size of between 120 mesh and 325 mesh. The refractory flour is fused  $\text{SiO}_2$ .

Three backup binder slurries were prepared according to Table I below. The Nyacol® 830 (NYA) system is a fiber and polymer free system distributed by Ransom & Randolph, the Customcote™ binder (CUS) manufactured by Ransom & Randolph is a fiber free polymer containing system and the CSB is the said binder containing fiber and polymer.

Table I: Formulas and viscosity ranges of the three slurries

System ID→	NYA	CUS	CSB
Binder	Nyacol® 830*	Customcote™ Binder	back-up binder composition of Example 4
Refractory, Loading	Ranco-Sil -140F, 63% loading	Ranco-Sil -140F, 63% loading	Ranco-Sil -140F, 62% loading
Viscosity	13 - 15 sec, #4 Zahn Cup	10 - 12 sec, #4 Zahn Cup	23 - 25 sec, #4 Zahn Cup

\* Diluted with water to have a binder solids being 25.0%.

All slurries were used to build test bar specimens for green strength determination. All systems used a 30x50 fused silica stucco sand.

The green bending properties are shown in Table II. For reference all data has been made relative to the NYA system at three backup coats and a seal dip (i.e. this point is equal to 1.0).

Table II: Relative Green bending properties of the three systems with various coats

Property→ System↓		Thickness	Green MOR	Green AFL
3 Coats + Seal	NYA	1.00	1.00	1.00
	CUS	0.94	1.63	1.46
	CSB	1.44	2.83	5.92
4 Coats + Seal	NYA	1.19	1.55	2.20
	CUS	1.20	2.03	2.97
	CSB	1.78	2.98	9.50
5 Coats + Seal	NYA	1.44	1.70	3.56
	CUS	1.35	2.46	4.53
	CSB	2.10	3.29	14.72

From Table II it can be seen that the Green MOR and AFL of the CSB system at three coats, 2.83 and 5.92 respectively, is greater than the same value for the NYA and CUS system at 4 and 5 backup coats. This indicates 3 backup coats of the CSB slurry will replace 4 and 5 backup coats of the NYA and CUS slurry.

Fibers useful in investment casting shell-mold compositions in accordance with the invention are organic and inorganic fibers. Most preferably inorganic fibers. Most preferably fibers useful in investment casting shell-mold compositions in accordance with the invention have an average length to diameter ratio of more than 30.

Particles useful in investment casting shell-mold compositions in accordance with the invention are organic and inorganic particles. Most preferably inorganic particles. Preferably particles useful in investment casting shell-mold compositions in accordance with the invention have an average largest diameter of less than 1 micron. Most preferably particles useful in investment casting shell-mold compositions in accordance with the invention have an average largest diameter of less than 0.5 micron.

While the invention has been described in terms of various preferred embodiments, those skilled in the art will recognize that various changes and modifications can be made without departing from the spirit and scope of the invention, as defined in the appended claims.

What is claimed is:

1. An investment casting shell-mold composition comprising:
  - a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles,
    - 1-20 percent by weight organic polymer, and
    - 0.1 to 70 percent by weight of inorganic fibers;
  - said inorganic particles having an average particle size smaller than 600 mesh, said inorganic fibers having an average length to diameter ratio of more than 30.
2. The composition according to claim 1, further comprising 1 to 90 percent by weight refractory powder.
3. The composition according to claim 2, wherein the refractory powder has a mesh size in the range of 120 to 400 mesh and said refractory powder is selected from the group consisting of alumino-silicates, fused silica, quartz silica, alumina, zircon, and zirconia;
4. The composition according to claim 1 wherein said colloidal sol comprises silica having an average particle diameter of 3 to 100 nanometers.
5. The composition according to claim 1 wherein the ratio of colloidal silica to latex polymer is greater than 1:1.
6. The composition according to claim 1 wherein said ratio ranges from 10:1 to 1:1, colloid:latex.
7. The composition according to claim 1 wherein said latex polymer includes a blend of acrylic polymers having a pH in the range of from 6 to 11; a viscosity in the range of

from 50 to 1000 centipoise; a solids content of from 40 to 65percent; and an average particle size of from 0.05 to 1.0 microns.

8. The composition according to claim 1 wherein said latex polymer includes a blend of acrylic polymers having a pH of from 7 to 10; a viscosity of from 50 to 500; a solids content of from 50 to 60percent; and an average particle size of from 0.1 to 0.5 microns.
9. The composition according to claim 1 wherein the polymer latex is an acrylic latex or a styrene butadiene latex.
10. The composition according to claim 1, wherein said silica sol has an average particle size of less than 30 nanometers.
11. The composition according to claim 1, wherein said latex polymer is an elastomeric latex polymer.
12. The composition according to claim 1, further comprising 1 to 98 percent by weight water.
13. A method of forming a shell mold, comprising the steps of
  - providing an investment casting shell-mold composition comprising:
    - a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles,
      - 1-20 percent by weight organic polymer, and
      - 0.1 to 70 percent by weight of inorganic fibers;
    - said inorganic particles having an average particle size smaller than 600 mesh, said inorganic fibers having an average length to diameter ratio of more than 30,
  - providing a disposable pattern,

mixing refractory flour and said binder composition to form a slurry composition,

applying said slurry composition to said pattern to form a slurry coating on said slurry coated pattern,

applying refractory stucco to said slurry coating to form a slurry and stucco pattern coating.

14. The method of claim 13 wherein said refractory flour has a particle size of from 120 to 400 mesh.
15. In method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a liquid binder composition; mixing refractory flour with the binder to form a slurry composition, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a partial slurry coating on said pattern, draining at least a portion of said liquid from said partial slurry coating to form a drained partial slurry coating,  
applying the slurry composition to said drained partial slurry coating to form a wet slurry coating, draining at least a portion of said liquid from said wet slurry coating to form a drained slurry coating and applying refractory stucco material to said drained slurry coating to form a refractory stucco and slurry coating, the improvement wherein said liquid binder composition comprises 0.1 to 70 percent by weight of inorganic fibers.
- 16 The method of claim 15 wherein said liquid binder composition further comprises 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer, and said refractory flour comprises inorganic particles having an average particle size smaller than 600 mesh.



17 The method of claim 15 wherein said inorganic fibers have an average length to diameter ratio of more than 30.

18. The method of claim 15 wherein said applying said composition to said pattern to form a slurry coated pattern, and said applying refractory stucco to said slurry coated pattern are repeated after drying.

19. A method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising 0.1 to 70 percent by weight inorganic fibers, providing a disposable pattern, applying said composition to said pattern to form a binder coated pattern, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating, the improvement wherein said binder composition comprises.

20. The method of claim 19 wherein said investment casting shell-mold composition further comprises 1-20 percent by weight organic polymer.

21. A shell mold formed by the process comprising: providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; and 0.1 to 70 percent by weight of inorganic fibers applying refractory flour to the binder to form a slurry, providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a slurry coated pattern, draining and applying a dry coarse refractory stucco layer.

22. In method of forming a shell mold, comprising providing an investment casting shell-mold composition comprising a back-up binder composition

comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; providing a disposable pattern, applying said composition to said pattern to form a binder coated pattern having a binder coating, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating, the improvement comprising adding 0.1 to 70 percent by weight of inorganic fibers to said back-up binder composition to form a fiber containing back-up binder composition .

23. The method of claim 22 wherein said back-up binder composition has a green Modulus of Rupture (MOR), and said fiber containing back-up binder composition has a green Modulus of Rupture (MOR) at least 25 percent greater than said back-up binder composition green Modulus of Rupture (MOR).
24. The method of claim 22 wherein said back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 75 percent greater than said back-up binder composition green adjusted fracture load (AFL).
- 25 The method of claim 23 wherein said back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 75 percent greater than said back-up binder composition green adjusted fracture load (AFL).
- 26 The method of claim 22 wherein a fiber free binder coating is formed as said binder coating except without said fiber, and is at least 25 percent thinner than said binder coating formed from said fiber containing back-up binder composition.
27. The method of claim 22 wherein said back-up binder composition has a green Modulus of Rupture (MOR), and said fiber containing back-up binder

composition has a green Modulus of Rupture (MOR) at least 35 percent greater than said back-up binder composition green Modulus of Rupture (MOR).

28. The method of claim 22 wherein said back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 100 percent greater than said back-up binder composition green adjusted fracture load (AFL).

29. The method of claim 22 wherein said back-up binder composition has a green Modulus of Rupture (MOR), and said fiber containing back-up binder composition has a green Modulus of Rupture (MOR) at least 50 percent greater than said back-up binder composition green Modulus of Rupture (MOR).

30. The method of claim 22 wherein said back-up binder composition has a green adjusted fracture load (AFL), and said fiber containing back-up binder composition has a green adjusted fracture load (AFL) is at least 150 percent greater than said back-up binder composition green adjusted fracture load (AFL).

31 The method of claim 22 wherein a fiber free binder coating is formed as said binder coating except without said fiber, and said fiber free binder coating is at least 33 percent thinner than said binder coating formed from said fiber containing back-up binder composition.

32 The method of claim 22 wherein a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Modulus of Rupture and said binder and flour pattern coating has a fiber containing green Modulus of Rupture at least 50 percent greater than said fiber free green Modulus of Rupture.

- 33 The method of claim 22 wherein a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Adjusted Fracture Load and said binder and flour pattern coating has a fiber containing green Adjusted Fracture Load at least 150 percent greater than said fiber free green Modulus of Rupture.
- 34 The method of claim 22 wherein a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Modulus of Rupture and said binder and flour pattern coating has a fiber containing green Modulus of Rupture at least 25 percent greater than said fiber free green Modulus of Rupture.
- 35 The method of claim 22 wherein a fiber free binder coating is formed as said binder coating except without said fiber having a fiber free green Adjusted Fracture Load and said binder and flour pattern coating has a fiber containing green Adjusted Fracture Load at least 100 percent greater than said fiber free green Modulus of Rupture.
36. A shell mold formed by the process comprising: providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of a colloidal sol comprising inorganic particles, 1-20 percent by weight organic polymer; and 0.1 to 70 percent by weight of inorganic fibers applying said composition to a pattern to form a binder coated pattern, applying refractory flour to said binder coated pattern to form a binder and flour pattern coating and firing said binder and flour pattern coating to form a shell mold.
37. A green shell mold formed by the process comprising: providing an investment casting shell-mold composition comprising a binder composition comprising a mixture of 20-98 percent by weight of inorganic particles, 1-20 percent by weight organic polymer; and 0.1 to 70 percent by weight of inorganic fibers, mixing refractory flour and the binder to form a slurry composition,

providing a primary coated disposable pattern, applying the slurry composition to the pattern to form a wet slurry coating on said pattern, draining at least a portion of said water from said wet slurry coating to form a drained slurry coating, applying a coarse refractory stucco to said drained slurry coating and removing said pattern from said drained slurry coating to form a green shell mold.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/12571

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B22C1/16 B22C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 01, 28 February 1995 (1995-02-28) & JP 06 277794 A (DAIDO STEEL CO LTD), 4 October 1994 (1994-10-04) abstract	15,22
Y	---	1-14
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 01, 28 February 1995 (1995-02-28) & JP 06 277795 A (DAIDO STEEL CO LTD), 4 October 1994 (1994-10-04) abstract	15,22
Y	---	1-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/12571

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 638 379 A (REMET CORP) 15 February 1995 (1995-02-15) abstract page 5, line 13 -page 6, line 32 example 1 claims ----	1-14
A	US 3 668 168 A (SELF JAMES M) 6 June 1972 (1972-06-06) example 1 column 2, line 74 -column 3, line 2 ----	
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Information on patent family members

International Application No

PCT/US 00/12571

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